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Raman and infrared spectra, conformational stability, *ab initio* calculations, and r_0 structural parameters of some organo-amines and hydrazines

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bstract The Raman and/or infrared (3500 to 50 cm^{-1}) spectra of some gaseous, liquid and solid organo-amines and methyl substituted drazines have been recorded Additionally, variable temperature (-55 to -150°C) infrared studies of several of these molecules dissolved in liquid non and/or krypton have been recorded and the enthalpy differences determined for the molecules which have conformers present at ambient mperature Utilizing low frequency spectral data along with the enthalpy differences, the potential functions governing the conformational changes have been obtained The geometric parameters, harmonic force constants, vibrational frequencies, Raman activities and depolarization infrared intensities, and energy differences, have been obtained from MP2(full)/6-31G(d) *ab initio* calculations Additionally structural parameters d energies have been obtained from MP2(full)/6-311G(d,p) and MP2(full)/6-311G(2d,2p) calculations as well as the corresponding ones with diffuse nctions The predicted quantities are compared to the experimental ones when appropriate For several of the molecules, the r_0 structural quantities ve been obtained by combining *ab initio* MP2(full)/6-311+G(d,p) predicted parameters with previously reported microwave rotational constants

eywords Raman and infrared spectra, conformational stability, *ab initio* calculations, organo-amines and hydrazines

MCS Nos. 33.20.Ea, 33.20.Fb, 33.15.Bh, 61.20.Gy

Introduction

ittle over a decade ago, Groner and Durig [1] reviewed the olecular dynamics of organonitrogen compounds from a brational and rotational spectroscopic perspective. It is clear om the material in this review that there were a significant umber of scientific problems for the organo-amines and ydrazines which were not completely solved or two or more esults were available that they were frequently in conflict. To ddress some of these problems, about three years ago we began n investigation of the vibrational spectra of a number of organo-mines and methyl-hydrazines. The goals of this research effort ere multi-fold and some of them will be listed, after which we hall provide a progress report on our attempts to solve some of problems associated with the molecular dynamics of these anonitrogen compounds.

Most of the previous studies on the conformational stabilities rgano-amines and methyl-hydrazines were conducted in the uid phase or in solutions with solvents like CS_2 and CCl_4.

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However the resulting conformational stabilities may not agree with the ones in gas phase, because of the difference among conformations in their tendency toward intermolecular hydrogen-bond formation in the condensed phases as well as the difference in interaction with the solvent molecules in solution phase. To address these problems, we have conducted conformational stability studies on these organonitrogen compounds in dilute (10^{-4} to 10^{-3} mol/L) low-temperature rare gas (krytpon −105 to − 150°C and/or xenon −55 to −100°C) solutions. The advantages of this approach lies in the fact that rare gas atoms have little association with solute molecules and the low concentration of such solutions greatly reduces the possibility of hydrogen bond formation among solute molecules. The cell path lengths utilized for the rare gas solutions were either 4 cm for the 400 to 3500 cm^{-1} range or 7 cm for the low wavenumber range of 50 to 600 cm^{-1}. Thus, the conformational stabilities obtained from the rare gas solutions are expected to be very close to those in the gas phase [2-6]. In addition, free from rotational fine structure, infrared bands in low temperature rare gas solutions have much smoother and more symmetric contours and their widths are greatly reduced, so that bands

arising from the less stable conformers can be more confidently assigned and better-separated from those due to the most stable rotamer, which makes the enthalpy difference determination much more reliable

Through a series of recent studies, we have found that *ab initio* calculations may incorrectly predict conformational stabilities with full electron correlation and reasonably large basis sets, especially with diffuse functions. A case in point is the 3-fluoropropene (allyl fluoride) molecule, the *cis* form (fluorine atom *cis* to the double bond) is experimentally determined to be more stable than the *gauche* form by 60 ± 8 cm^{-1} (0.72 ± 0.10 kJ/mol) in liquid xenon and 81 ± 1 cm^{-1} (0.97 ± 0.01 kJ/mol) in liquid argon [7]. However, *ab initio* calculation utilizing the MΦller-Plesset perturbation method [8] to the second order with a relatively large Pople basis set with diffuse functions such as MP2/6-311++G(d,p) predicts the *gauche* form to be more stable by 117 cm^{-1} (1.40 kJ/mol). Quadratic configuration method with singles and doubles utilizing the same basis set QCISD/6-311++G(d,p) also gives the *gauche* to be more stable by 50 cm^{-1} (0.60 kJ/mol). Similarly, Dunning augmented basis set MP2/aug-cc-PVDZ predicts the *gauche* rotamer to be more stable by 117 cm^{-1} (1.40 kJ/mol). Galabov *et al.* [9] have concluded the inclusion of diffuse functions significantly increases the stability of the *gauche* conformer relative to the *cis* form, sometimes resulting in an incorrect energetic ordering for allyl fluoride. This effect is reduced with increasing size of basis sets applied. The question arises as what is the origin of the problem and whether molecules with non-bonded pairs on some of the atoms may have a similar preference. Therefore, the difference in predicted energies for the organoamines with and without diffuse function was investigated.

We have encountered the similar problems with organoamine and methyl-hydrazine molecules. For the ethylamine molecule, the *trans* form is experimentally determined to be more stable than the *gauche* form by 70 ± 6 cm^{-1} (0.84 ± 0.07 kJ/mol) in liquid krypton and 80 ± 6 cm^{-1} (0.96 ± 0.07 kJ/mol) in liquid xenon. However, *ab initio* calculations at the MP2/6-31+G(d), MP2/6-311+G(d,p), MP2/6-311+G(2d,2p) and MP2/6-311+G(2df,2pd) levels predict the *gauche* form more stable by 65, 64, 66 and 59 cm^{-1}, respectively. Such erroneous *ab initio* preference for the *gauche* stability also exists for the allylamine molecule in our study which will be addressed in detail in the discussion section.

McKean [10] has shown that the "isolated" C-H stretching frequency can be used to obtain excellent ground state C-H distances. The plot of the ν_{CH} frequencies versus the determined r_0 C-H distances results in the equation $r_0 = 1.3982 - 0.0001023\ \nu^0_{CH}$ for the determination of r_0 value. The predictive power of the correlation based on the gradient of the resulting line, shows that 10 cm^{-1} corresponds to 0.001Å, which is supported by the precision of the ν^0_{CH} data [10]. The predicted value should be good to ± 0.0005Å, which is limited by the variation in ν^0_{CH} frequency due to possible coupling of this mode with other motions in the molecule, which should not exceed 5 cm^{-1}! Therefore, from "isolated" CH stretching frequencies, distances to an accuracy of 0.001Å should be obtained. Similarly, linear relation between the Si – H and Ge-H "isolated" frequencies and their corresponding ground state r_0 distances have been established. The significance of such studies lies in the fact that the derived M-H (M = C, Si, Ge) distances are more accurate and reliable than many of those reported microwave data. However, microwave spectroscopy provides the most precise technique for obtaining bond distances for most molecules in the gas phase, with most of the bond distances for M-H bonds being obtained by this method. The two different types of M-H bond distances usually obtained are the r_0 and r_s distances, where the r_0 value depends on the microwave-determined molecular rotational constants, and the r_s distance (s standing form substitution) depends on the substitution of each atom in the molecule. Since the r_s distance is closer to the equilibrium bond distance, r_e, and because deuterium is readily available, many of the reported M-H bond distances are r_s values. However, the determination of the r_s bond distances requires the determination of the coordinates of each atom in the three-dimensional rotational coordinate system and frequently the hydrogen atom lies near one of the axes which results in a near-zero value and a poorly determined coordinate for the hydrogen atoms. In some cases, even a negative value has been obtained for the hydrogen atom! The microwave literature is full of reported C-H bond distances that are totally unrealistic r_s values, but these values were not questioned until the recent use of ν^0_{CH} frequencies has shown them to be in error. Such problems may also exist for the reported N-H distances. However there is no information on the N-H "isolated" frequency and the resulting predicted ground state r_0 (N-H) distances. Thus, we have initiated studies toward this direction with a series of secondary amines and mono-deuterated primary amine molecules.

Good structural parameters can be obtained of organic molecules by adjusting the structural parameters from *ab initio* MP2/6-311+G(d,p) or MP2/6-311G(d,p) calculations to fit the experimental rotational constants obtained from microwave data [11-15]. To solve the problem with limited number of isotopomers, in an effort to reduce the number of independent variables, we classify the structural parameters into sets according to their types, *i.e.* bond (of the same bond order) lengths connecting the same elements in the same set keeping their relative ratio, bond angles connecting the same type of bonds in another set keeping their difference in degrees, and similar dihedral angles in a set of their own keeping their difference in degrees. The validity of such partition of similar structural parameters into different sets is under the assumption that the errors from *ab initio* calculations are systematic [7]. With the reliable C-H distances derived from the above mentioned "isolated" stretching frequencies [10], we [16] have shown the MP2/6-311+G(d,p) *ab initio* calculations give C-H distances for

substituted hydrocarbons to 0.002Å of these values. Thus, we are able to further reduce the number of independent variables by fixing these parameters to the *ab initio* predicted values. Therefore, excellent adjusted r_0 structures for the heavy atoms can be obtained, with the fitted rotational constants within usually less than one MHz from the microwave data.

For many primary amines, the NH_2 twisting mode has not been confidently identified in the gas spectrum, largely due to their extremely low infrared intensities (often 2-3 magnitudes smaller than other modes), however by using scaled *ab initio* frequencies along with the study of the infrared spectra in rare gas solutions, the annealed solid, the Raman spectra as wells as those of the NHD and ND_2 isotopomers, we are able to confidently assign these fundamental vibrations for a number of primary amine molecules.The enthalpy for the hydrogen bonding in organoamines and methyl-hydrazines are also questionable. There is a serious question whether the second virial coefficient can be used to obtain the enthalpy of hydrogen bonding which probably gives a value too large. We have assigned distinctive shoulders on bands or separate bands arising from hydrogen bonding and determined the enthalpy of hydrogen bonding for a number of these nitrogen-containing molecules. The results of these Raman, infrared and theoretical studies are reported herein.

2. Experimental

The allylamine (stated purity 99%), ethylmethylamine (stated purity 97%) and ethylamine (stated purity 98%) samples were purchased from Aldrich Chemical Co., Milwaukee, WI. The sample of methylhydrazine was obtained commercially and distilled at its normal boiling point (86-88°C). The sample N-methylpropargyl amine was prepared by the reaction of propargyl amine and methyl iodide in alcohol in a sealed tube. The product N methylpropargyl amine hydroiodide salt was treated with potassium hydroxide to produce the free amine. Further purifications of all of the samples were carried out with a low-temperature, low-pressure vacuum fractionation column. The purity of the samples were checked by GC-MS and comparing the mid-infrared spectrum of the vapor to that previously published where available

The Raman spectra were recorded on one of the three instruments with most of the data taken with a Spex model 1403 spectrophotometer equipped with a Spectra-Physics model 164 argon ion laser operating on the 5145 Å line. The laser power used was 0.5 w with slit widths of 3 cm^{-1}. The spectra of the liquids and solids were recorded with the samples contained in a sealed capillary tube. Also used was a Cary model 82 spectrophotometer equipped with a spectra-Physics model 171 argon laser operated at 5145Å and a Bruker model FRA 106 Fourier transform spectrometer equipped with YAG-MAX LASER C-95 (CVI Co.) source.

The mid-infrared spectra of gaseous and solid samples were obtained using a Perkin-Elmer model 2000 Fourier transform spectrometer equipped with a nichrome wire source, a Ge/CsI beamsplitter, and a DTGS detector. The spectra of the gas were obtained by using a 10 cm cell fitted with CsI windows. The spectra of the solid were obtained by condensing the sample on a CsI substrate held at ~77 K by boiling liquid nitrogen, housed in a vacuum cell fitted with CsI windows. The samples were repeatedly annealed until no further changes were observed in the spectrum. The theoretical resolution used to obtain the spectra of both the gas and the solid was 1.0 cm^{-1}.

The mid-infrared spectra of the samples dissolved in liquefied krypton and/or xenon as a function of temperature were recorded on a Bruker model IFS-66 Fourier transform spectrometer equipped with a globar source, a Ge/KBr beamsplitter, and a DTGS detector. The temperature studies ranged from -105 to -150°C for krypton and -55 to -100°C for xenon and were performed in specially designed cryostat cells consisting of a 4 or 7 cm path length copper cell with wedged silicon windows sealed to the cell with indium gaskets. The complete system is attached to a pressure manifold to allow for the filling and evacuation of the cell. The cell is cooled by liquid nitrogen and the temperature is monitored by two Pt thermoresistors. Once the cell is cooled to a designated temperature, a small amount of sample is condensed into the cell. The system is then pressurized with the rare gas, which immediately starts to condense, allowing the compound to dissolve. For each temperature investigated, 100 interferograms were recorded at a 1.0 cm^{-1} resolution, averaged, and transformed with a boxcar truncation function.

3. *Ab initio* calculations

The LCAO-MO-SCF restricted Hartree-Fock calculations or calculation with electron correlation at the MP2 level [8] were performed with the Gaussian-98 program using Gaussian-type basis functions [17]. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all the geometric parameters using the gradient method of Pulay [18].

In order to obtain a complete description of the molecular motions involved in the normal modes, normal coordinate analyses were carried out. The force fields in Cartesian coordinates was obtained with the Gaussian 98 program from the MP2/6-31G(d) calculation. The internal coordinates were used to form the symmetry coordinates. The B-matrix elements were used to convert the *ab initio* force field from Cartesian coordinates into the force field in desired internal coordinate [19]. The resulting force constants were used to reproduce the *ab initio* vibrational frequencies for all different conformers. The diagonal elements of the force fields in internal coordinates were then modified with scaling factors. The geometrical averages were utilized for the off-diagonal force constants. Each calculation was repeated to obtain the fixed scaled force field and scaled vibrational frequencies and potential energy distributions (P.E.D.).

We calculated the theoretical Raman spectra with the Raman scattering activities obtained from the *ab initio* MP2/6-31G(d)

calculations. The evaluation of the Raman activity using the analytical gradient method has been developed [20,21]. The activity S_j can be expressed as $S_j = g_j(45\alpha_j^2 + 7\beta_j^2)$, where g_j is the degeneracy of the vibrational mode j, α_j is the derivative of the isotropic polarizability, and β_j is that of the anisotropic polarizability The Raman scattering cross sections, $\partial\sigma_j/\partial\Omega$, which are proportional to the Raman intensities, can be calculated from the scattering activities and the predicted wavenumber for each normal mode [22,23]. To obtain the polarized Raman cross sections, the polarizabilities are incorporated into S_j by $S_j[(1-\rho_j)/(1+\rho_j)]$, where ρ_j is the depolarization ratio of the j^{th} normal mode. The Raman scattering cross sections and the calculated scaled frequencies were used together with the Lorentzian function to obtain the calculated spectra The infrared spectra were predicted from the MP2/6-31G(d) calculations The predicted scaled frequencies were used together with a Lorentzian function to obtain the calculated spectra. Infrared intensities were calculated based on the dipole moment derivatives with respect to the Cartesian coordinates. The derivatives were taken from the *ab initio* calculations transformed to normal coordinates by.

$$\frac{\partial\mu\alpha}{\partial Qi}\Big| = \sum_i \left|\frac{\partial\mu\alpha}{\partial Q_j}\right| Lij$$

The Q_i is the i^{th} normal coordinate, X_j is the j^{th} Cartesian displacement coordinate, and L_{ij} is the transformation matrix between the Cartesian displacement coordinates and normal coordinates The infrared intensities were then calculated by:

$$I_i = \frac{N\pi}{3c^2}\left[\left(\frac{\partial\mu_x}{\partial Q_i}\right)^2 + \left(\frac{\partial\mu_y}{\partial Q_i}\right)^2 + \left(\frac{\partial\mu_z}{\partial Q_i}\right)^2\right]$$

4. Results and discussion

As an indication of the progress being made to obtain some of the goals of the research listed earlier, we shall now provide some of the results for individual molecules For all of the molecules studied to date, all but one has conformers present at ambient temperature. Also for most of them there have been some microwave data so structural parameters have been obtained by combining the *ab initio* predicted parameters with the rotational constants

Ethylmethylamine - This secondary amine, $CH_3CH_2NHCH_3$, has three conformers present at ambient temperature. These conformers are shown in Figure 1 where the one with the two methyl groups are 180° from each other are indicated as T (Me-*trans*) with the other two as *gauche* forms The *gauche* conformer indicated as G (LP-*trans*) has the lone pair on the nitrogen atom *trans* to the methyl group whereas the *G'* (H-*trans*) form has the H atom *trans* to the methyl group.

In an earlier low-frequency (below 530 cm^{-1} spectral investigation [24] of ethylmethyl- amine, utilizing both gaseous infrared and Raman spectroscopy, two series of methyl torsional modes were observed in the Raman spectrum with one observed at 249 cm^{-1} and the other one at 217 cm^{-1}. A third one was observed in the infrared spectrum beginning at 215.6 cm^{-1} which was assigned to the T conformer. The ones observed in the Raman spectrum were assigned to the two *gauche* forms. This assignment was based on the fact that stronger Raman scattering was observed for the methyl torsions than the absorption in the infrared spectrum for the methyl torsions for the *gauche* conformers of both ethylamine [25] and n-butane [26]. These assignments gave barriers of 1153 and 1091 cm^{-1} for the methyl groups for the T conformer and 1343 and 1142 cm^{-1} for the two *gauche* forms.

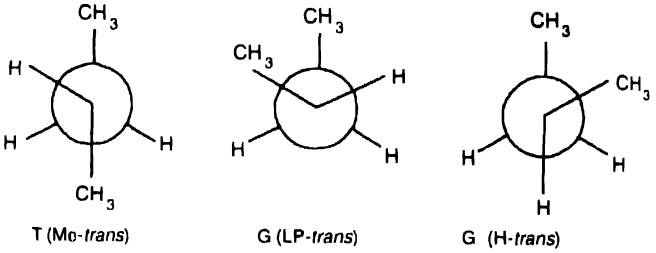


Figure 1. The *trans* conformer and the *gauche* conformers of ethylmethylamine viewed along the N-C bond

From a relatively recent *ab initio* investigation [27] of the internal rotations in ethylmethylamine utilizing a rather small basis set of 3-21G(N*) with fully optimized geometries at the Hartree-Fock level, the authors conclude that the larger methyl rotational barriers should correspond to the T conformer. These authors [28] also carried out a conformational stability study by a variable temperature Raman study of the liquid and obtained enthalpy differences of 384 ± 25 cm^{-1} (4.6 ± 0.3 kJ/mol) and 300 ± 25 cm^{-1} (3.6 ± 0.3 kJ/mol) between the most stable T conformer and the least stable *G'* form and the second most stable *G* conformer, respectively. However the stability order for the two *gauche* conformers differed from the stability predictions from the *ab initio* calculations [28]. Since ethylmethylamine has significant hydrogen bonding in the liquid phase the authors [28] ascribed the different stability order for the two *gauche* forms from the predicted *ab initio* order as arising from the greater tendency toward hydrogen bonding in the *G* conformer

Therefore as a continuation of our conformation stability studies we carried out variable temperature infrared studies of krypton solutions of ethylmethylamine to determine the relative stability of the three conformers [29]. Additionally, we have obtained from *ab initio* calculations at the MP2 level the harmonic force fields, infrared intensities, Raman activities, depolarization ratios, and vibrational frequencies with a larger basis set 6-31G(d) with full electron correlation. We also carried out *ab initio* calculations with the 6-311G(d,p), 6-31+G(d,p), 6-311G(2d,2p) and 6-311+G(2d,2p) basis sets with full electron

correlation by the perturbation method to second order [8] to obtain the optimized geometries and conformational stabilities for all three conformers. Conformational stabilities have also been obtained from density functional theory (DFT) calculations by the B3LYP method with the same basis sets for comparison with the MP2 predictions.

In Table 1 are listed the *ab initio* calculations utilizing a variety of basis sets and these data clearly indicate that the most stable conformer is the T form and the second most stable one is the *G'* (H-*trans*) conformer with an energy difference between the last two of nearly 200 cm^{-1}. This order is the same as predicted earlier with the small basis set at the Hartree-Fock level [27]. Also it should be noted that the preference for the *G* form when the lone pair is *trans* to the carbon-carbon double bond is only in the range of ~ 50 cm^{-1} with a larger energy difference between this form and the *trans* rotamer when diffuse functions are used. However for the *G'* form it varies both ways depending on the size of the basis set.

Table 1. Calculated energies and energy difference for several conformations of ethylmethylamine by *ab initio* and hybrid DFT methods

Method/basis	Energy (Hartree)	Energy differences (cm^{-1})	
	T	*G*	*G*
RHF/6-31G(d)	173.276489	410	517
MP2(full)/6-31G(d)	-173.851684	311	405
MP2(full)/6-31+G(d)	-173.863197	268	486
MP2(full)/6-311G(d,p)	-174.046639	270	406
MP2(full)/6-311+G(d,p)	-174.052907	253	463
MP2(full)/6-311G(2d,2p)	-174.100926	224	413
MP2(full)/6-311+G(2d,2p)	-174.105912	251	460
MP2(full)/6-311+G(2df,2pd)	-174.176277	259	464
B3LYP/6-31G(d)	-174.479529	211	468
B3LYP/6-31+G(d)	-174.487986	343	503
B3LYP/6-311G(d,p)	-174.532999	333	444
B3LYP/6-311+G(d,p)	-174.536899	322	481
B3LYP/6-311+G(2d,2p)	-174.544778	333	505
B3LYP/6-311+G(2df,2pd)	-174.549167	339	505

We also calculated the barriers to internal rotation of the two methyl groups with three different basis sets 6-31G(d), 6-311+G(d,p) and 6-311+G(2d,2p) at the MP2 level with full electron correlations. For the T conformer the values for the CH_3 – C rotor was 1244, 1181 and 1170 cm^{-1}, respectively, and the CH_3 – N rotor was 1230, 1107 and 1073 cm^{-1}, respectively. For both the G and G' forms the barriers for the CH_3 – C rotor were about 100 cm^{-1} from each basis set, i.e. 1123, 1082 and 1058 cm^{-1} for the G' form and about 150 cm^{-1} for the CH_3 – N rotor with values of 1047, 968 and 917 cm^{-1} for the G' form. Therefore the earlier assignment of the relatively strong Raman torsional transitions (Figure 2) must be due to the T conformer rather than to the *gauche* conformers.

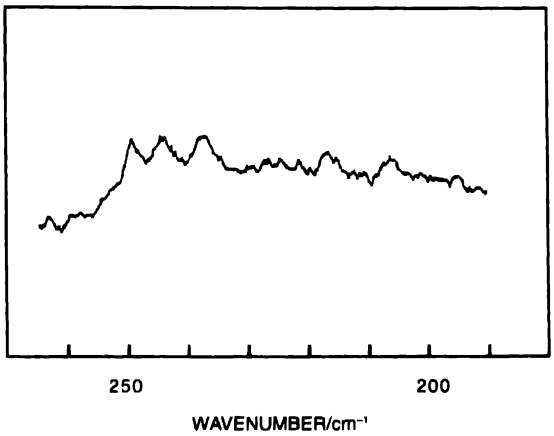


Figure 2. Raman spectrum of gaseous ethylmethylamine between 270 and 180 cm^{-1} recorded with 500-torr pressure and 3-cm^{-1} spectral bandwidth.

We have found by a series of studies [31-35] that the *ab initio* MP2/6-31G(d) calculations predict the methyl barriers rather well, i.e. usually better than with 100 cm^{-1} of the experimental values. In the earlier torsional study the barriers were calculated by the coupled two-top model [36] which gave barriers of 1342 and 1143 cm^{-1} for the CH_3 – C and CH_3 – N rotors, respectively, which are 100 cm^{-1} higher for the CH_3 – C top and 100 cm^{-1} lower for the CH_3 – N rotor compared to the *ab initio* MP2/6-31G(d) predicted values. We also calculated the barriers from the torsional frequencies without top-top coupling and obtained values of V_3 = 1338 and V_6 = -35 cm^{-1} for the CH_3 – C rotor and V_3 = 958 and V_6 = – 35 cm^{-1} for the CH_3 – N rotor. The value for the CH_3 – C rotor is essentially the same as the 1342 cm^{-1} obtained from the coupled rotor model but the one for the CH_3 – N rotor is nearly 200 cm^{-1} lower than obtained by the two top model. The potential energy distribution for these two rotors gives almost equal contribution for each of the torsional fundamentals with some contribution to the higher frequency mode of the CNC bend. Therefore the two rotor model [36] appears to be the more appropriate model for ethylmethylamine which indicates that the *ab initio* MP2/6-31G(d) calculations predicts barriers more consistent with the experimentally determined values than the calculations with the significantly larger basis sets.

In the earlier microwave investigation of ethylmethylamine, the investigators [30] obtained the inversion barrier for the Me-*trans* conformer from the tunnel splittings for both the normal and amino-d_1 isotopomers in the ground and heavy atom torsional excited states. For the normal species a barrier of 1818 cm^{-1}(5.2 kcal/mol) was reported [30] which was relatively independent of the heavy atom torsional state but for the N–d_1 species the tunneling is damped by the barrier but increases from 1633 cm^{-1} (4.67 kcal/mol) in the ground state to 1776 cm^{-1}

(5.08 kcal/mol) in the second excited state For this isotopomer the barrier appears to be approaching the value of 1818 cm^{-1} [30] which was obtained for the normal species. We calculated this inversion barrier utilizing a variety of basis sets at either the restricted Hartree-Fock and/or with full electron correlation at the MP2 level for all three conformers. For the T conformer the values ranged from a high value of 2358 cm^{-1} from the MP2/6-31G(d) calculation to a low value of 1944 cm^{-1} from the MP2/6-311+G(2d,2p) calculation. Since the value was decreasing with increased size of the basis set it is concluded that these *ab initio* calculations can provide barriers which are in agreement with the experimentally determined values from the microwave splitting data

As indicated earlier we have found that we can obtain good structural parameters by adjusting the structural parameters obtained from the *ab initio* calculations to fit the rotational constants obtained from the microwave experimental data Unfortunately, the microwave spectra of only the T conformer has been reported [30] for two isotopic species, *i.e.* the normal species and the N-d_1 isotopomer. Therefore, there are only six rotational constants available so only six structural parameters can be determined Therefore the four distances (C–H, C–N, C–C, N–H) and two heavy atom angles were determined. The parameters obtained by this method are listed in Table 2. It is estimated that these heavy atom distances should be accurate to ±0.005Å and the carbon-hydrogen distances to ±0.003Å. The angles are expected to be predicted to ±0.5° with the possible exception of the dihedral where the *ab initio* calculations are the least sensitive. The N-C distances have values similar to those reported for this parameter (1.462 ± 0.005Å) for dimethylamine [37] The fit of the six rotational constants is given in Table 2 and the agreement with the experimental rotational A constants is 2 and 4 MHz for the normal and N–d_1 species, respectively These differences are expected to be larger than those for the B and C rotational constants since these constants are larger by a factor of three than the B and C rotational constants. The four B and C rotational constants are fit to 1MHz or better for both isotopomers. Therefore, the fit is quite good and the adjusted r_0 parameters are probably as accurate as could be obtained from r_s parameters from microwave data or r_g parameters from electron diffraction data.

We also determined the enthalpy differences among the three conformers. From the variable temperature studies the difference were determined to be 335 ± 35 cm^{-1} (4.01 ± 0.42 kJ/mol) between the most stable T conformer and the least stable G rotamer. An enthalpy difference of 177 ± 27 cm^{-1} (2.12 ± 0.32 kJ/mol) was estimated between the G′ form and the most stable T conformer. These results are somewhat lower but still in reasonable agreement with the *ab initio* predictions at all levels of calculations (Table 1). It is estimated that there is only 12 ± 2% of the G form and 26 ± 3% of the G′ conformer present at ambient temperature.

Table 2. Structural parameters[a], rotational constants and dipole moments for the Me-*trans* conformer of ethylmethylamine.

Parameter	MP2/6-311+G(d,p)	Adjusted r_0
$r(C_1N_2)$	1.458	1.462
$r(C_3–N_2)$	1.457	1.461
$r(C_1–C_3)$	1.521	1.530
$r(C_3–H_6)$	1.093	1.094
$r(C_3–H_7)$	1.092	1.093
$r(C_3–H_8)$	1.095	1.095
$r(C_1–H_4)$	1.105	1.106
$r(C_1–H_5)$	1.096	1.096
$r(C_9–H_{10})$	1.103	1.103
$r(C_9–H_{11})$	1.094	1.094
$r(C_9–H_{12})$	1.092	1.093
$r(N_2–H_{13})$	1.016	1.017
$\angle C_3C_1N_2$	110.8	111.4
$\angle C_1N_2C_9$	112.4	112.1
$\angle H_6C_3C_1$	110.8	110.8*
$\angle H_7C_3C_1$	110.2	110.2*
$\angle H_8C_3C_1$	110.7	110.7*
$\angle H_4C_1N_2$	112.0	112.0*
$\angle H_5C_1N_2$	107.5	107.5*
$\angle H_{10}C_9N_2$	113.5	113.6*
$\angle H_{11}C_9N_2$	109.0	109.0*
$\angle H_{12}C_9N_2$	109.7	109.7*
$\angle H_{13}N_2C_1$	108.6	108.7*
$\tau(C_9N_2C_1C_3)$	176.9	
$\tau(H_{13}N_2C_1C_3)$	55.9	
A	26116	25938[b](23772)[c]
B	3937	3921[b](3904)[c]
C	3686	3668[b](3627)[c]

Bond distances in Å, bond angles in degrees, rotational constants in MHz and dipole moments in Debye, parameters marked with an asterisk were not adjusted.

Rotational constants , A = 25936, B = 3920, C = 3668 MHz for normal species and A = 23768, B = 3904, C = 3628 MHz for N-d species Ref [30]

Numbers in parentheses are rotational constants for the N-D species

In our earlier reported study [29] of ethylmethylamine we did not report the *ab initio* predicted Raman spectra. Therefore we have calculated the spectrum utilizing the experimentally determined enthalpy differences among the conformers. These spectra are shown in Figure 3. Since the recorded spectrum [28] is for the liquid one expects some significant differences between it and the predicted. This is particularly true since the G conformer is the second more stable form in the liquid rather than the G′ form found in the krypton solution. Nevertheless the agreement is considered except for the CCN bend at 447 cm^{-1} where the

Raman predicted intensity is only 1.9 Å^4/amu. The intensity is grossly under-predicted but some of the intensity maybe due to the condensed state. However even with this large deviation it is clear that the predicted spectra can be very useful for making vibrational assignments and identifying bands due to the less abundant conformers.

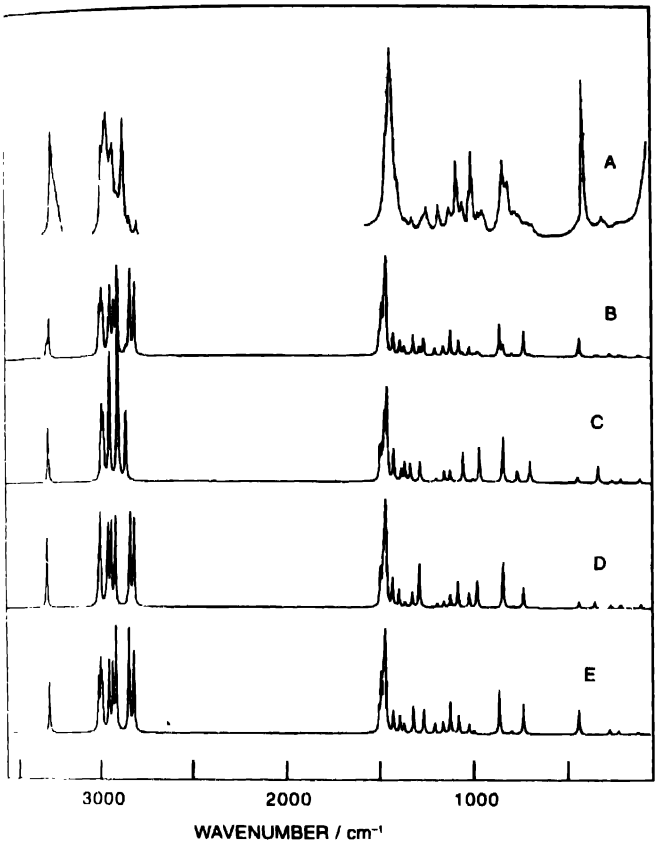


Figure 3. Raman spectra of ethylmethylamine (A) experimental spectrum of the liquid, (B) MP2/6-31G(d) *ab initio* calculated spectrum of T, G′ and 1 conformer mixture with experimental ΔH values of 177 cm^{-1} between G′ and T and 371 cm^{-1} between G and T conformers; (C) calculated for the pure G conformer; (D) calculated for the pure G′ conformer, (E) calculated for the pure T conformer.

N methylpropargyl amine - Another secondary amine which we recently studied [38] was N-methylpropargyl amine (4-aza-1-pentyne), HC ≡ CCH_2NHCH_3 (Figure 4), to evaluate the effect the propargyl group (—CH_2—C ≡ C—H) on the conformational stability of this molecule compared to the three conformer stabilities of ethylmethyl amine [27-29]. There had not been any previous vibrational spectroscopic studies of N-methylpropargyl amine, so we recorded the Raman spectra of the liquid and solid and the infrared spectra of the gas, krypton solutions at variable temperatures, and solid. We also carried out *ab initio* calculations employing the 6-31G(d) basis set at the level MΦller-Plesset to the second order (MP2) to obtain equilibrium geometries, force constants, vibrational frequencies, infrared intensities, Raman activities, and conformational stabilities. Structural parameters and conformational stabilities were also obtained from larger basis sets, *i.e.*, MP2/6-311+G(d,p) and MP2/6-211+G(2d,2p), as well as from density functional theory (DFT) utilizing several basis sets. We were particularly interested in the structural parameters since there had been an earlier microwave study of this molecule [31] which clearly indicated that the LP-*trans* conformer (Figure 4) was the most stable form.

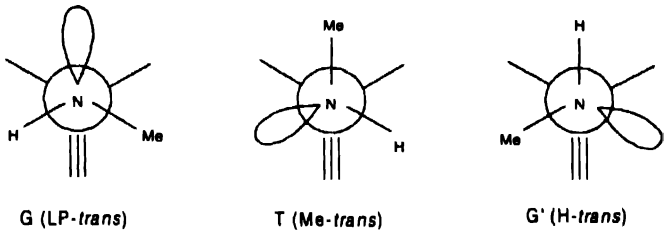


Figure 4. The *trans* and two *gauche* conformers of N-methylpropargyl amine

The vibrational assignment for the LP-*trans* conformer was confidently given since it is in such a large abundance in the gas phase and it is the only conformer remaining in the solid. However there are very large shifts between the frequencies for the fundamentals in the gas phase and those for the solid. These shifts arise from the hydrogen bonding as well as the shifts associated with the bending modes of the ethynyl, C ≡ C–H, group. Utilizing four scaling factors of 0.70 for CNH bend, 0.88 for the CH stretches, 0.90 for CH bends and heavy atom stretches, and 1.3 for C ≡ C–C and C ≡ C–H bends with the *ab initio* MP2/6-31G(d) predicted frequencies, the fundamentals of the LP-*trans* conformer are predicted with an average error of 10 cm^{-1} which represents a percentage error of less than 1%.

In the earlier microwave study [39], five excited vibrational states were assigned for the LP-*trans* conformer and from relative intensity measurements of the lines to those of the ground state the vibrational frequencies were determined. From the strongest of these lines (40% of the ground-state intensity) a frequency of 152 ± 20 cm^{-1} was obtained which was assigned to the heavy atom torsional mode. However this mode was clearly observed in the spectrum of the gas at about 120 cm^{-1} and predicted from the *ab initio* calculations in the range 120 to 124 cm^{-1}. Therefore it is expected that the estimated uncertainty was too conservative so that a difference of 32 cm^{-1} between the observed fundamental and the microwave predicted wavenumber is considered satisfactory. A second exited state of this mode was assigned from the microwave data but the bending mode at 170 cm^{-1} observed in the spectrum of the gas (171 cm^{-1} in the spectrum of the solid) was not assigned. This mode should have given the second most intense satellite lines in the microwave spectrum so they were either not recognized or the lines assigned to the second excited heavy atom torsional mode are due to this fundamental. The remaining three vibrationally exited state lines which were assigned had relative intensities of 25, 13, and 11% which yield wavenumbers of 222 ± 30, ~325, and ~356 cm^{-1} which were assigned as the methyl torsion and the two lowest frequency bending modes. These data are consistent

with the observed bands in the infrared spectrum of the gas at 240, 322 and 369 cm^{-1} although the latter two modes are the second and third lowest frequency bending motions. Therefore the agreement of the microwave predicted wavenumbers with the observed values is quite good except for the heavy atom torsion and the lowest frequency bending mode.

We calculated the inversion and methyl barriers utilizing the 6-31G(d) basis set at the levels of HF, MP2, and B3LYP. The predicted inversion barriers have similar values from the HF and B3LYP calculations whereas those from the MP2 calculations are 300 to 400 cm^{-1} larger than those from the HF and B3LYP calculations. Also it should be noted that the inversion barrier for the LP-*trans* form compared to the other enantiomer in the H-*trans* form is about 350 cm^{-1} irrespective of the level of calculation (Table 3). The methyl torsional barriers are predicted to be nearly the same (~1200 cm^{-1}) for the three conformers from the MP2/6-31G(d) calculations with only slightly larger spreads of 50 and 100 cm^{-1} from the B3LYP and HF calculations, respectively (Table 7). It is expected that the predicted barrier of 1200 cm^{-1} should be close to the actual barrier, i.e. within 100 cm^{-1}, based on comparison of measured and predicted barriers for a number of methyl rotors [32-36].

Table 3. Calculated energies and energy difference for three conformations of N-methylpropargyl amine by *ab initio* and hybrid DFT methods

Method/basis	Energies and energy differences		
	LP-*trans* (Hartree	Me-*trans* (cm^{-1})	H-*trans*[a] (cm^{-1})
RHF/6-31G(d)	-209.909856	394	566
MP2(full)/6-31G(d)	-210.580035	609	612
MP2(full)/6-31+G(d)	-210.618247	514	504
MP2(full)/6-311+G(d)	-210.760196	668	583
MP2(full)/6-311+G(d,p)	-210.815074	591	552
MP2(full)/6-311+G(2d,2p)	-210.873635	497	513
B3LYP/6-31G(d)	-211.300431	465	628
B3LYP/6-311+G(d)	-211.357955	355	542
B3LYP/6-311+G(d,p)	-211.370171	352	526
B3LYP/6-311+G(2d,2p)	-211.378179	313	486

[a] Energies of conformations relative to LP-*trans*

The experimental methyl barrier value was obtained from the observed splittings in the microwave spectrum [39] and the determined value is 1153 ± 33 cm^{-1} (13.79 ± 0.40 kJ/mol) which should be quite an accurate value since the separation of the microwave lines depend directly on the barrier height. However if one uses the methyl torsional frequency of 240 cm^{-1} from the infrared spectrum of the gas, a barrier of 1307 cm^{-1} is obtained by using the F number ($F = h^2/8\pi^2 I_r$ where I_r is the reduced moment of inertia for the internal rotation) from the determined structural parameters from this current study. This value is expected to be too high since ν_{28} the band assigned as the methyl torsion has a 17% contribution from the higher frequency $C \equiv C - C$ bend. Thus by using the methyl torsional frequency considerable error can arise if it is mixed with low frequency bending motions but such mixing is usually not found. Nevertheless it is clear that the *ab initio* MP2/6-31G(d) predicted value of 1194 cm^{-1} is in excellent agreement with the experimental value [39] of 1153 ± 33 cm^{-1}.

We also obtained the enthalpy differences among the conformers from variable temperature (−105 to −150°C) studies of the infrared spectra of the sample dissolved in liquid krypton. From these data the enthalpy difference were determined to be 360 ± 72 cm^{-1} (4.31 ± 0.86 kJ/mol), between the most stable LP-*trans* conformer and the second most stable Me-*trans* rotamer. An enthalpy difference of 100 ± 20 cm^{-1} is estimated between the Me-*trans* form and the least stable H-*trans* conformer. These results are in reasonable agreement with the *ab initio* predictions at all levels of calculations. It is estimated that there is only 8% of the H-*trans* form and 14% of the Me-*trans* conformer present at ambient temperature. However it should be noted that there was considerable difficulty encountered in determining the enthalpy differences among the conformers of N-methylpropargyl amine because of the hydrogen bonding of the molecule in the krypton solution. One of the measurements between the Me-*trans* and H-*trans* conformer gave a value of 86 cm^{-1} with the Me-*trans* form more stable whereas another pair gave a value of 127 cm^{-1} with both of them having relatively large uncertainties. Since the *ab initio* MP2 calculations predicted a difference in energy for these two conformers of only a few wavenumbers (16 cm^{-1} from the 6-311+G(2d,2p) basis set) it was not possible to confidently state that the Me-*trans* form is the second most stable conformer. The hydrogen bonding in the solution could affect the enthalpy determination differently for these two forms. Nevertheless we estimate that the ΔH difference is 100± 20 cm^{-1} based on the experimental results with the Me-*trans* form more stable than the H-*trans* rotamer based on the relative conformational stability of these two forms for ethylmethylamine [30]. As indicated earlier however, the Me-*trans* conformer is the most stable form in ethylmethylamine rather than the LP-*trans* form for N-methylpropargyl amine. One possible explanation for the LP-*trans* form being more stable than the Me-*trans* form in N-methylpropargyl amine could be its more favored orientation towards conjugation. The two least stable conformers for N-methylpropargyl amine have C_1N_1 distances which are 0.006 and 0.009Å longer than the corresponding bond length for the LP-*trans* conformer. For ethylmethylamine the comparable distances only differ by 0.001Å.

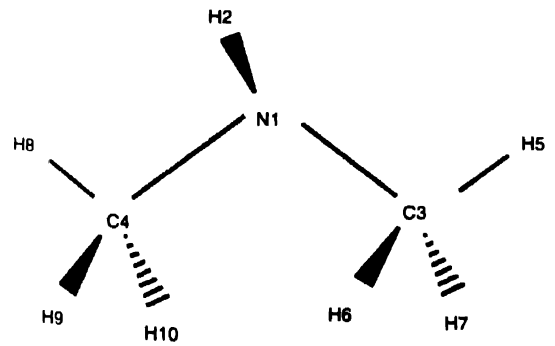
Dimethylamine - Another secondary amine which we are currently investigating is dimethylamine, $(CH_3)_2NH$, where we are interested in the barrier to methyl rotation and the structural parameters both of which have been previously addressed [37, 40]. Therefore we carried out *ab initio* calculations at the MP2 level with four different basis sets and the predicted structural parameters are listed in Table 4. Also listed in Table 4 are the

able 4. Structural parameters (distances in Å, angles in degrees), dipole oments (Debye) and total energy (Hartree) for dimethylamine

rameter	MP2/6-31G(d)	MP2/6-311 + G(d,p)	MP2/6-311 + G(2d,2p)	MP2/6-311 + (2df,2pd)
C_4–N)	1.456	1 456	1.456	1.450
$(C_4$–$H_{8,9})$	1 092	1 092	1.085	1.086
C_4 $H_{9,10})$	1.103	1 103	1.095	1 098
C_3 $H_{6,7})$	1.094	1.094	1 086	1 088
N H)	1.018	1 014	1.008	1 010
(C NC_4)	111.7	111 9	111 7	111.7
$(C_3$NH)	108 8	109 2	109 3	109 5
$(NC_4H_{8,9})$	109 5	109 8	109 9	110.0
$(NC_4H_{9,10})$	114 1	113.6	113.6	113 6
$(NC_4H_{7,10})$	108.9	108 9	108 9	109.0
C_4NHC_3)	121 9	122 7	122 5	122 8
$H_{8,9}C_4NH$)	±56 3	±55 9	±55 3	±55 1
$H_{9,10}C_4NH_{5,6}$)	±121 9	±121 8	±121 9	±122 0
$H_{9,10}C_4NH_{6,7}$)	±117 8	±118 0	±118.0	±118 0
	34235	34338	34479	34540
	9414	9403	9445	9497
	8288	8281	8308	8352
μ_a	0 000	0 000	0 000	0 000
μ_b			0 408	0 382
μ_c			1 086	1 072
μ_t	1 221	1.205	1 160	1 138
(F + 134)	0 678102	0 835370	0 876808	0.931079

Ref [37]

reviously reported structure which were obtained from the microwave data [37]. First it should be noted that all three hydrogens on the methyl group are non-equivalent and that one of them is predicted to be significantly longer (~0.009Å) han the other two from all of the *ab initio* calculations and the lifference is about the same irrespective of the basis set size. In he microwave study [37] the assumption that the $C_3 - H_6$ listance (Figure 5) was the same as the $C_3 - H_7$ distance is



gure 5. Dimethylamine with atom numbers.

wrong and leads to incorrect carbon-hydrogen distances. We have used the six rotational constants from the normal and ^{15}N species and adjusted the predicted parameters from the *ab initio* MP2/6-311+G(d,p) calculation and these adjusted r_0 values are listed in Table 4. The C-H distances 1.092, 1.094 and 1.103Å are shorter than the values of 1.095, 1.098 and 1.108Å obtained from isolated carbon-hydrogen stretching frequencies [41] which may be slightly too long. Nevertheless the less the order is predicted correctly and with an expected uncertainty of 0.003Å are nearly in agreement with the values reported from the carbon-hydrogen stretching frequencies.

The inversion barrier and barrier to methyl rotation were calculated at both the RHF and MP2 levels with the latter calculations with three different basis sets (Table 5). The

Table 5. Methyl rotational barrier and nitrogen inversion barrier of dimethylamine.

Method/Basis Set	Ground State Energy (Hatree)	Me Rotational Barrier Energy (Hatree)	Barrier (cm^{-1})
RHF/6-31G(d)	-134 238850	-134.233111	1260
MP2/6-31G(d)	-134 678102	-134.671760	1392
MP2/6-311+G(d,p)	-134.835370	-134.829634	1259
MP2/6-311+G(2d,2p)	-134.876808	-134 871334	1201
MP2/6-311+G(2df,2pd)	-134.931079	-134.925489	1227

inversion barrier varied from a low value of 1789 cm^{-1} to a high value of 2247 cm^{-1} from the MP2/6-31G(d) calculation. The reported experimental value [37] of 4.1 ± 1.1 kcal/mol (1433 ± 385 cm^{-1} agrees with the lowest predicted value but is significantly lower than the highest predicted value. A similar problem also exists for the barrier to methyl rotation where the experimental value [40] of 1052 ± 12 cm^{-1} is much lower than the predicted values of 1201 to 1392 cm^{-1} which is the range obtained from the *ab initio* calculations. There can be no doubt concerning the assignment of the torsional transitions since both the A´ and

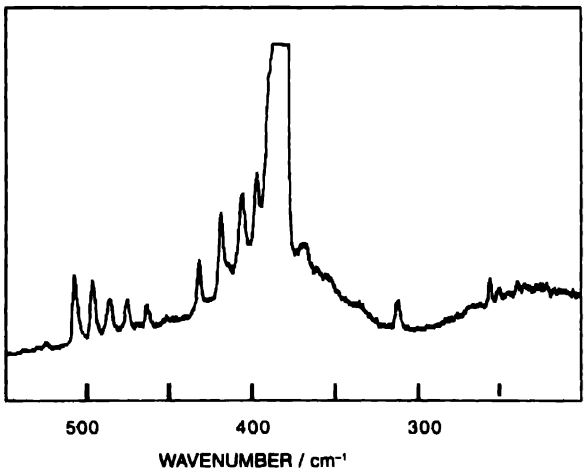


Figure 6. Raman spectrum of gaseous dimethylamine showing overtones with "hot bands" of the two torsional modes.

A'' modes are clearly observed as overtones with many "hot bands" in the Raman spectrum of the gas (Figure 6). Also the barrier was obtained from microwave splitting data in the first excited state of the torsional mode from several isotopic species [42] and the value of 1126 ± 7 cm^{-1} (3.22 ± 0.02 kcal/mol) is significantly lower than the predicted value of 1392 cm^{-1} from the MP2/6-31G(d) calculations which have been shown [31-35] to give good results for hydrocarbons and organosilanes.

Allylamine (3-aminopropene) - We have also investigated a number of primary amines with one of the first ones allylamine, CH_2 = $CHCH_2NH_2$ where there are possibly five conformers present at ambient temperature (Figure 7). The microwave spectra had been reported for four (Ct, Gt, Gg and Cg) of these conformers [43-47] with the first one reported for the Ct conformer [43]. For the normal species of this conformer the reported [43] A, B and C rotational constants differ by only 9, 11 and 9 MHz, respectively, from those predicted from the *ab initio* MP2(full)/6-311+G(d,p) calculations. This initial agreement indicated that at this level of *ab initio* calculation it would be possible to predict the r_0 structural parameters for all four of the conformers which has been done [48]. Our major interest in allylamine was the conformational stability since a significant amount of the earlier studies dependent upon the predictions from *ab initio* calculations utilizing a relative small basis set [49-52]. Therefore we carried out *ab initio* calculations utilizing several different basis sets both with and without diffuse functions as well as density functional theory (DFT) calculations by the B3LYP method. The results of these calculations are listed in Table 6 and there are significant variations in the results. From the *ab initio* MP2(full) calculations with the diffuse functions 6-311+G(2d,2p) and 6-311+G(2df,2pd) the conformation stability order is Ct > Gg > Gt > Cg > Gg' whereas with the smaller basis set 6-311+G(d,p) the Ct conformer is less stable than both the Gt and Gg forms so the order becomes Gg > Gt > Ct > Cg > Gg' where the first indicator is for the relative position of the amino group (C = *cis* or G = *gauche*) to the double bond (rotation around the C–C bond) and the second one (*t* = *trans*, *g* = *gauche*, *g'* = *gauche'* is the relative position of the amino rotor, i.e. rotation around the C-N bond. This same order is predicted from the DFT calculations with all three of these basis sets by the B3LYP method but with very small differences. However with the two largest basis sets without diffuse functions, 6-311G(2d,2p) and 6-311G(2df,2pd), the *ab initio* calculations predict the conformer stability order to be Ct > Cg > Gt > Gg > Gg' whereas with the smaller basis set 6-31G(d) the order is Ct > Gt > Gg > Cg > Gg'. Utilization of diffuse functions for the *ab initio* calculations gives a distinctive preference for the *gauche* conformer for both the amino torsion and the relative position

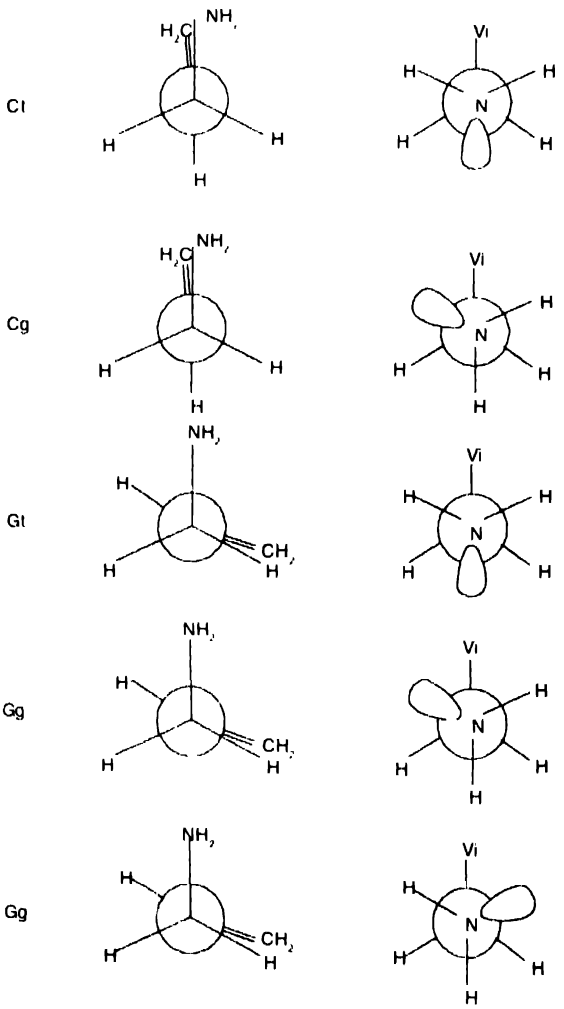


Figure 7. The five possible conformers of allyl amine where the capital letters C (*Cis*) and G (*Gauche*) indicate the relative position of the amino group to the double bond and the second letter (lower case) t (*trans*), g (*gauche*) or *g'* (*gauche'*) the relative position of the amino rotor

Table 6. Calculated energies and energy difference for the five conformations[a] of allyl amine by *ab initio* and hybrid DFT

Method/basis& Energy (E_h)	Energy differences[b] (cm^{-1})				
	Ct	Cg	Gt	Gg	Gg'
MP2(full)/6-31G(d)	-172.653908	263	95	108	793
MP2(full)/6-311G(d,p)	-172.834537	252	112	197	817
MP2(full)/6-311+G(d,p)	-172.841799	116	-36	-111	502
MP2(full)/6-311G(2d,2p)	-172.887007	180	212	240	904
MP2(full)/6-311+G(2d,2p)	-172.893297	126	82	7	604
MP2(full)/6-311G(2df,2pd)	-172.954817	188	260	281	933
MP2(full)/6-311+G(2df,2pd)	-172.960389	131	110	42	628
B3LYP/6-31G(d)	-173.247733	349	95	215	921
B3LYP/6-311G(d,p)	-173.304708	289	133	251	950
B3LYP/6-311+G(d,p)	-173.309660	170	0	-13	617
B3LYP/6-311+G(2d,2p)	-173.317458	168	-3	-10	578
B3LYP/6-311G(2df,2pd)	-173.317257	221	133	29	872
B3LYP/6-311+G(2df,2pd)	-173.322037	163	6	-4	576

Conformation labels. Ct = *cis-trans*, Cg = *cis-gauche*, Gt = *gauche-trans*, Gg = *gauche-gauche*-1, Gg' = *gauche-gauche*-2. [b]Energies of conformations relative to Ct (*cis-trans*), a negative number indicates the conformer is more stable.

of the NH_2 group to the double bond. Therefore it is not possible to predict the conformer stability order from the *ab initio* calculations. However these data do indicate that the Gg′ conformer has a very large ΔH and there is little possibility of observing fundamentals due to it. Also the Gt and Gg conformers probably have similar ΔH values with the Ct from the most stable rotamer with the major question whether the Cg conformer is more or less stable than the Gt and Gg conformers.

Therefore we carried out variable temperature (−55 to −150°C) studies of the infrared spectra (3500 to 60 cm^{-1}), of the sample dissolved in liquid krypton and/or liquid xenon. From these data it has been possible to identify four of the possible five stable conformers as well as to determine their relative stabilities. The order of the conformers stabilities has been determined to be Ct, Gt < Gg, Cg and Gg′. The enthalpy differences have been determined between the most stable Ct conformer and the second most stable rotamer, Gt, to be 92 ± 8 cm^{-1} (1.10 ± 0.10 kJ/mol), and the third most stable rotamer, Gg, to be 122 ± 12 cm^{-1} (1.46 ± 0.14 kJ/mol) with the Cg having a significant larger value of 173 ± 12 cm^{-1} (2.07 ± 0.14 kJ/mol) than either of these forms. No evidence was obtained for the fifth conformer Gg′ which is predicted by most of the *ab initio* calculations to be less stable by more than 600 cm^{-1} than the Ct form. The percentage of each conformer at ambient temperature is estimated to be: Ct (23%), Gt (29%), Gg (25%) and Cg (20%).

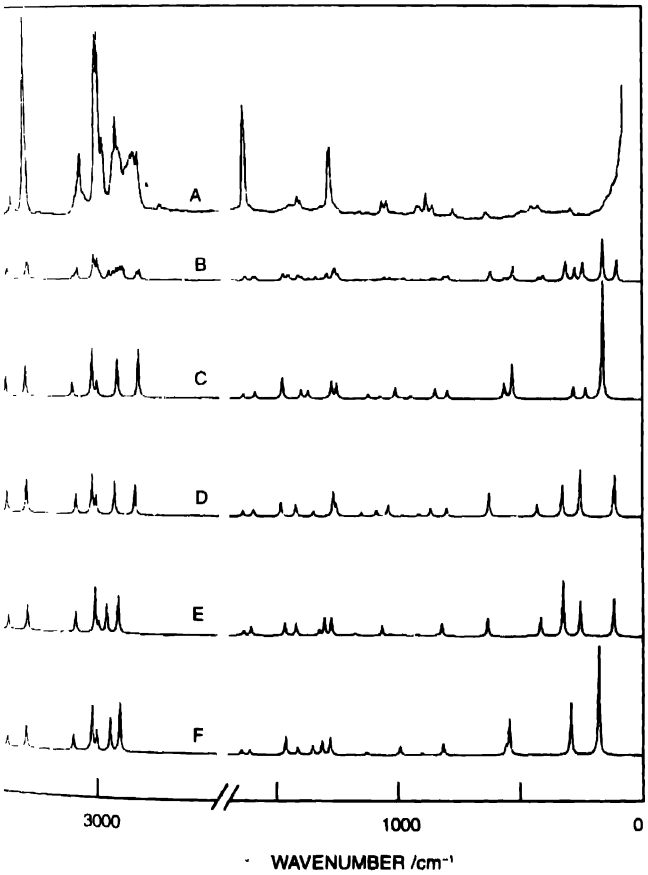


Figure 8. Raman spectra of allyl amine: (A) liquid at room temperature, (B) simulated spectrum of a mixture of the four conformers with ΔH of 0 cm^{-1} for Gt, ΔH of 122 cm^{-1} for Gg, and ΔH of 173 cm^{-1} for Cg relative to the most stable Ct form; (C) calculated spectrum for pure Cg, (D) calculated spectrum for pure Gg; (E) calculated spectrum for pure Gt, (F) calculated spectrum for pure Ct.

We utilized these enthalpy difference along with the predicted frequencies and Raman activities to predict the Raman spectra from *ab initio* MP2/6-31G(d) calculations. These spectra are shown in Figure 8 and the predicted one is in reasonable agreement with the observed spectrum when it is taken into account that it is a liquid with extensive hydrogen bonding. Nevertheless the spectrum was quite valuable for identifying the four different conformer lines.

Several other primary amines are currently being investigated with the study of ethylamine nearly complete. There is also a problem with the use of diffuse functions for the *ab initio* calculations where the incorrect conformer is predicted to be the more stable form.

Methylhydrazine - The methylhydrazine molecule CH_3NHNH_2 was the first of several methylhydrazines which we are currently investigating. There had been several conformational studies [53-59] of methyl hydrazine and it is clear that the *inner* conformer (methyl group between the two hydrogen atoms of the NH_2 group) is more stable than the *outer* form (hydrogen atom attached to N-CH_3 between the two hydrogen atoms of the NH_2 group). Thus our interest was to determine the enthalpy difference between the *inner* and *outer* forms as well as obtain information on the hydrogen bonding. Therefore we recorded the variable temperature FT-IR spectra of xenon solutions of methyl hydrazine. Additionally we carried out *ab initio* calculations utilizing the 6-31G(d) basis set at the level of restricted Hartree-Fock and/or with full electron correlation by the perturbation method to second order to determine the optimized structural parameters, harmonic force constants, vibrational frequencies, infrared intensities, Raman activities, and conformational stabilities. We have also calculated the structural parameters and conformational stabilities utilizing the larger 6-311+G(d,p) and 6-311+G(2d,2p) basis sets at the MP2 level as well as density functional theory (DFT) calculations with all three of the basis sets. The results of these spectroscopic and theoretical studies were recently published [60]. The enthalpy difference was determined to be 323 ± 30 cm^{-1} (3.86 ± 0.36 kJ/mol) with the *inner* conformer (methyl group staggered and between the two hydrogens of the NH_2 group) the more stable rotamer. A complete vibrational assignment was presented for the *inner* conformer, and several of the fundamentals of the *outer* conformer were assigned. These assignments were consistent with the predicted wavenumbers obtained from *ab initio* MP2/6-31G(d) calculations utilizing three scaling factors. It was also possible to obtain the enthalpy value for the hydrogen bond from the relative intensity of a band at 745 cm^{-1} to a fundamental at 890 cm^{-1} of the more stable conformer. The determined value was 282 ± 19 cm^{-1} which was approximately one-half of the value obtained for the hydrogen bond in methylamine [61].

Several other methylhydrazines such as 1,1-dimethylhydrazine and 1,2-dimethylhydrazine are currently being investigated to determine the conformer stabilities, structural parameters, barriers to rotation, etc The spectroscopic and theoretical results for these molecules will be published in due course.

Acknowledgment

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